ON THE X-RAY LUMINESCENCE SPECTRA OF THALLIUM-ACTIVATED ALKALI HALIDE CRYSTALS *

By APARESH CHATTERJEE

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Plate XI

ABSTRACT. The X ray luminescence spectra of thallium-activated alkali halides have been investigated at ordinary and low temperatures The band systems are of two types, the visible part is due to the lattice emission, while the short wavelength part exhibits characteristic thallium emission The lattice bands gain in intensity due to the presence of thallium. The intensity of the characteristic band is linearly related to the concentration of thallium. It has been shown that Seitz's explanation of the characteristic thallium band emission is inadequate, and an alternative energy level scheme has been proposed

INTRODUCTION

Since initiated by Pohl and his associates, the thallium-activated alkali halide crystal phosphors occupy an unique place in phosphor research. These substances gave a clue to an attempt of understanding correctly the luminescence processes in crystals in general The absorption spectra were studied by Hilsch and Pohl (1928, followed by many papers), and Förio (1929). An early explanation of absorption was given by Seitz (1938, 1939), who attributed the absorption peaks at 195, 205, 247·5 $m\mu$ for KCl-Tl to the electronic transitions $^1S_0 \rightarrow {}^3P_1$, $^1S_0 \rightarrow {}^1P_2$, and $^1S_0 \rightarrow {}^1P_1$ of the thallium ions modified by the Madelung field in a lattice. Fialkovskaya (1948*a*) has reported another temperature-insensitive weak absorption band (at 273 $m\mu$ for KCl-Tl, and at 300 $m\mu$ for KBr-Tl) at high thallium concentrations detectable only in thick single crystals. Koch (1929) has shown that thallium is monatomically dispersed in the lattice.

The emission spectra of these phosphors have been studied by von Meyeren (1930), Bünger (1930), Flechsig (1930), Fromherz (1931), Bünger and Flechsig (1931), Pringsheim (1942), Fialkovskaya (1948*b*), Hutten and Pringsheim (1948), Shalimova (1948), Bose and Sharma (1950) A report of the earlier work may be found in articles by Hilsch (1937) and Rees (1942); the older literature deals exclusively with emission of the phosphors by using ultraviolet excitation.

Thallium may be introduced in the lattice of the alkali halides by fusion, or by electrolytic dispersion, or by evaporation from a concentrated solution

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(Pringsheim, 1942) or by prolonged grinding of the thallous salts (Hutten and Pringsheim, 1948); the negative ion of the thallous salt is of little consequence in forming such mixed crystals. Perturbations in the original lattice due to the excess of positive ions from ideal stoichiometric proportions are produced in such impurity crystals.

PRESENT WORK

The luminescence spectra of alkali halides activated by thallium have been recently investigated by Bose and Sharma (1950) under cathode rays. The samples were prepared by melting the mixture of weighed quantities of TlCl and the alkali halide at about 900°C. The present investigations were carried out by using the same phosphors under X-ray excitation to confirm and supplement their measurements.

The amount of thallium present in the phosphors is given as the percentage weight of TlCl dissolved in 100 gms of alkali halides, and not as molar ratios. For recording the spectra at liquid oxygen temperatures, a special sample holder was constructed, as shown in Fig. 1. Other experimental arrangements have already been described (Chatterjee, 1950, henceforth referred to as Paper I).

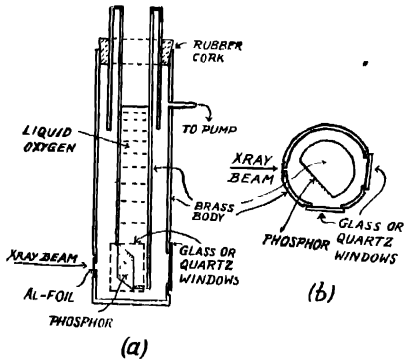
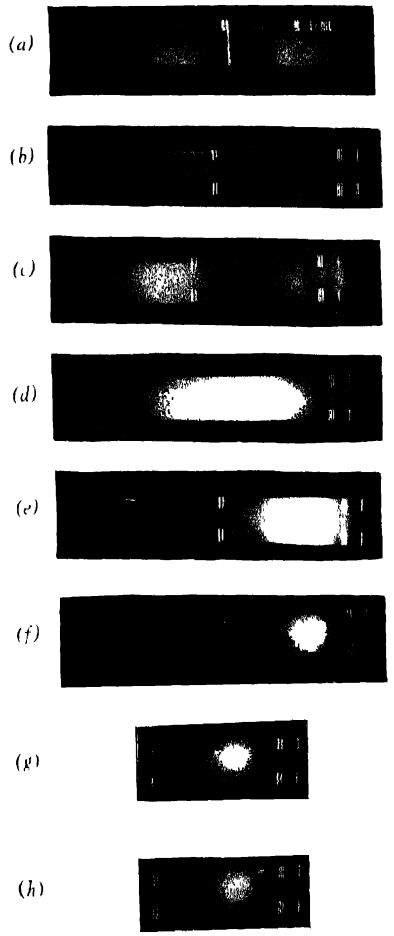


FIG. 1 –
Low temperature phospor holder
(a) Longitudical Section, (b) Transverse section near the bottom.

The spectra are shown in Plate XI the microphotometer traces in Fig. 2, and the measurements in Table I. Since the measurements are inaccurate by ±20 AU at 300 $m\mu$, and no systematic shifts in the room temperature (25°C) and low temperature (−180°C) spectra were found, only the low temperature data are given.

NATURE OF THE EMISSION BANDS

Comparing the present data with those of other workers, it may look surprising that in almost all cases the longer wavelength bands are completely



X-ray luminescence spectra of thallium-activated alkali halides.
(*a*) NaCl-Tl(1%), (*b*) NaBr-Tl(2.5%), (*c*) KCl-Tl(2.5%)
(*d*) KBr-Tl(2.5%), (*e*) KI-Tl (2.5%), long exposure; (*f*) KI-Tl(2.5%)
short exposure, (*g*) KI-Tl (5%), (*h*) KI-Tl (0.1%)

absent, and visible luminescence has been entirely overlooked. For the convenience of comparision, the older work is summarized in Table II.

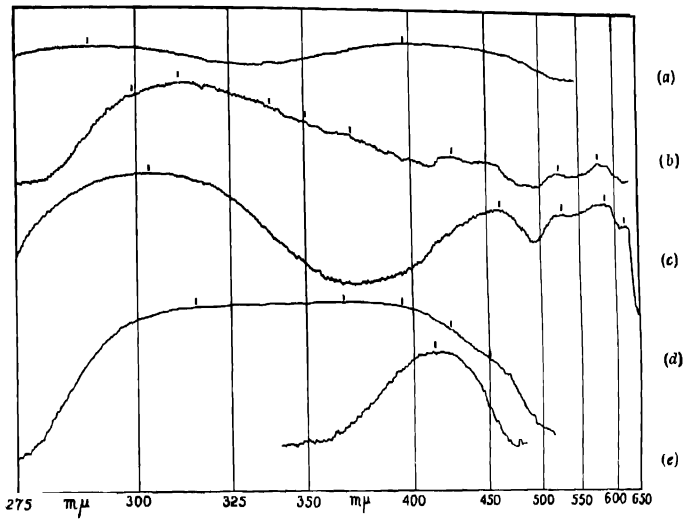


FIG. 2

Microphotometer traces of luminescence spectra (reduced) (*a*) NaCl-Tl (1.0%); (*b*) NaBr-Tl (2.5%); (*c*) KCl-Tl (2.5%), (*d*) KBr-Tl (2.5%); (*e*) KI-Tl (0.5%).

TABLE I

X-Ray Luminescence Spectra of Thallium Activated Alkali Halides

Phosphor	Approximate ranges in $m\mu$	peak positions in $m\mu$
NaCl–Tl (1.0%)	496–350	396.5
	305–270	289.0 (Tl)
NaBr–Tl (2.5%)	600–505	575, 530
	470–440	450
	400–280	425, 366.5, 350.5, 337(?), 310
	continuous	299.0 (Tl)
KCl–Tl (2.5%)	650–500	617, 583.5, 523.5
	500–405	460.5
	340–280	303.0 (Tl)
KBr–Tl (2.5%)	500–275 continuous with peaks difficult to locate.	450, 422 394, 366 315 (Tl)
KI–Tl (0.5%)	660–510 continuous, very faint	537, 520
	470–360	419.5 (Tl)

TABLE II

Emission of Tl-activated phosphors using ultraviolet light

Phosphor	von Meyeren (1930) 150°C, 20°C—180°C Peaks in $m\mu$			Bunger and Flechsing (1931)	Pringsheim (1942) Extensions	Hutten and Pringsheim (1948) Peaks
NaCl-Tl	290,	288,	286	288		
NaBr-Tl	315, 298,	308, 295,	305 295			
KCl-Tl				370	600-560 500-430 405-360	610, 540 457 385
	304,	298,	296	300	330-280	300
KBr-Tl					600-520 430-340	
	320, 297,	350, 319,	360 311	350 318	360-310	325
KI-Tl	301,	415,	427	—	—	
RbCl-Tl	317,	315,	314	—	—	

When the present work is compared with those of the workers of Pohl's school, it is found that the shortest wavelength bands of our measurement coincide with theirs: these near ultraviolet emission bands are attributed to the thallium present in the lattice as impurity, and hence are characteristic of thallium. But the X-ray luminescence spectra show also a number of bands extending far into the visible region, sometimes covering the whole range. The origin of these longer wavelength bands must necessarily be due to some other causes *not* associated with thallium, and there are only two possibilities: they may well be due to the presence of other impurities, or due to the emission of the parent lattice itself.

In Paper I, we have shown that the X-ray luminescence spectra of pure alkali halides show lattice emission, and if we compare the spectra of pure phosphors with these thallium-activated ones, we can verify that the longer wavelength band patterns and peaks are very closely similar in shape and position in the two cases. We thus arrive at the very important conclusion that the longer wavelength bands owe their origin to the radiative transitions taking place in the original lattice, and are *not* due to any impurities. These phosphors strikingly demonstrate the characteristic emission and the lattice emission side by side

Pringsheim (1942) and Hutten and Pringsheim (1948) have observed such a phenomenon; in fact, they were first to demonstrate clearly that the

phosphors under consideration show a visible luminescence. However, we are now in a position to account for both ultraviolet and visible luminescence of these phosphors.

From Plate XI, it can be verified that to a first approximation, the bands of the parent lattice are not much affected in position (*cf.* Paper I), except that occasional overlapping, omissions, and enhancements of the weaker bands occur in a few cases.

The characteristic thallium band changes to longer wavelength side with increasing lattice constant of the parent matrix.

The intensity of the thallium band depends on the crystal . it is more for crystals of greater lattice constant, resulting in lesser exposure in recording the spectra. This fact indicates that the emission of the phosphor is also dependent on the case with which the thallium ions (having large ionic radii) enter the lattice

Generally, the characteristic thallium emission is more intense than the lattice emission. This is especially true for low thallium content, and is the most important reason why earlier workers did not get visible luminescence by using molar thallium concentrations of the order of 01 to .05%. On short exposures, only the thallium band is obtained, in a few cases (*e.g.*, KI-Tl, See Plate XI, Figs. *e* and *f*), while on long exposures, the lattice bands appear at their appropriate positions, but the thallium band is much widened at the same time.

Though the lattice emission bands do not change in position, they distinctly gain in intensity due to the presence of thallium. This may be exemplified by citing the case of KCl-Tl A measurably good luminescence spectrum of pure KCl could not be obtained even on an exposure of 20 hours, but KCl-Tl (2.5%) showed the lattice emission bands in 4 hours very distinctly. The lattice bands of pure KBr (*cf* Paper I) terminate at 455 $m\mu$, but the bands are just measurable from that region in case of KBr-Tl ; the weaker lattice bands are enhanced due to the presence of thallium. Another additional proof, though indirect but significant, may be given from Pringsheim's data. It is well known that pure alkali halides *never* fluoresce under ultraviolet excitation, but Pringsheim has prepared thallium-activated phosphors which show visible luminescence quite well under ultraviolet arc. Hence thallium behaves truly as an 'activator' of the lattice emission

It appears that thallium emits a single band. Though older workers have reported two bands in a few cases, it can be easily verified that one of these bands, particularly the longer ones (at 470 $m\mu$ for KCl-Tl, Bünger and Flechsig, and at 305 $m\mu$ for NaBr-Tl, von Meyeren) is due to the parent lattice (Bose and Sharma, 1950).

The spectra at low temperatures did not show any special features. The lattice bands were not much affected in position and intensity, but the thallium bands were sharpened. No systematic shifts were found.

INTENSITY VARIATION OF THE CHARACTERISTIC BAND WITH CONCENTRATION

Hutten and Pringsheim state that at low thallium concentrations, KCl-Tl flouresce violet, while with increasing concentrations, the overall fluorescence efficiency increases and extends far into regions of longer wavelengths. To study the intensity variation of the thallium band, KI-Tl phosphors were prepared from melt with 0.1% and 5.0% TlCl (0.07 and 3.35 mol per cent Tl). A linear law was tacitly assumed, and proportional exposores were given, The 0.1% phosphor was exposed for 200 minutes, and the 5% sample for 4.5 minutes. Densitometric measurements were made with the microphotometer, as shown in Fig. 3.

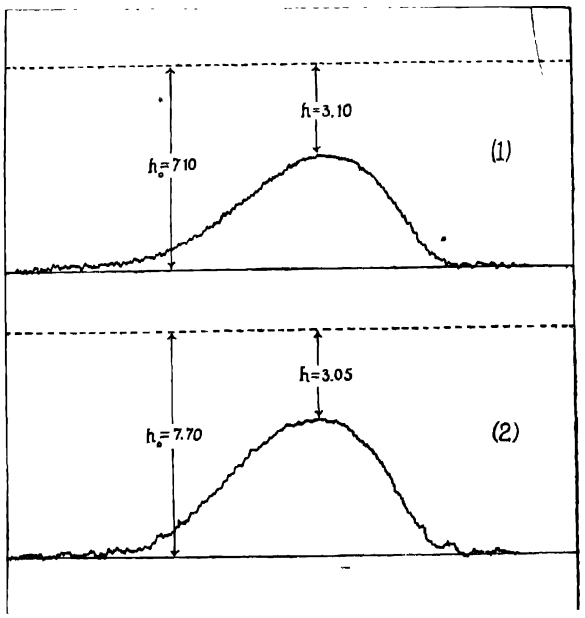


FIG. 3

"Intensity curves of KI-Tl phosphors (reduced to half size,.
(1) 5% phosphor, 4.5 minutes; (2) 0.1% phosphor 200 minutes.
The values of h and h_0 are in cms. (see text)."

The concentration n and the photographic density of blackening d are related to the intensity of emission I by the relation

$$n.t=I=I_0e^{-\mu d}, \quad \text{or} \quad n.t/I'_0=e^{-d}, \ (I'_0=I_0e^{-\mu}), \tag{1}$$

where t is the time of exposure. If h be the microphotometer height, then

$$h = h_0 e^{-d}, \qquad \ldots (2)$$

defined by $h = h_0$ (base lines of Fig. 3) when $d = 0$, and $h = 0$ (top dotted lines) for $d = \infty$. Equating (1) and (2), we get

$$(nt)/I'_0 = h/h_0, \qquad \ldots (3)$$

If there be two concentrations n_1 and n_2 exposed for t_1 and t_2 under identical conditions, then $(I'_0)_1 = (I'_0)_2$, and

$$\frac{n_1 t_1}{n_2 t_2} = \left(\frac{h}{h_0}\right)_1 \Big/ \left(\frac{h}{h_0}\right)_2 \qquad \ldots (4)$$

Putting numerical values, the left hand side gives 1·125 and the right hand side from Fig. 3 gives 1·102. Thus the agreement is within 2%. Considering the various uncertainties, the most important one being the difficulty of obtaining a desired steady X-ray current from a Hadding tube at a predetermined voltage in both cases, the agreement is much better than expected. We can conclude that the intensity of characteristic thallium emission is linearly related to its concentration in the parent lattice.

CARRIERS OF LUMINESCENCE

Some controversy has recently arisen as to the carriers of luminescence in thallium-activated alkali halides. Seitz (1938) is of opinion that Tl^+ ions enter the lattice in place of vacant positive ion sites, and the levels of ionized thallium are so modified in the lattice field as to give the $^1P_{1,2} \rightarrow {}^1S_0$ emission transitions in the near ultraviolet. But Pringsheim (1942), from the similarity of the absorption spectra in solution and in the solid state, and Hutten and Pringsheim (1948), from the X-ray diffraction photographs, are in favour of complex formation of the type (TlX_n)—(*cf.* Kröger, 1948, p 53). Whatever be the correct explanation, Pringsheim has rightly pointed out

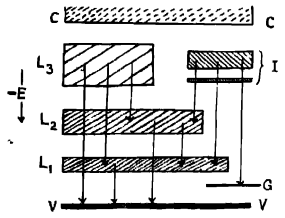


FIG. 4

A new energy level scheme for thallium activated alkali halides. V = valence band (normally filled, combined p levels of halogens, as modified in a lattice field); C = conduction band, normally empty; L_1, L_2,..., ionic exciton levels, G = ground state of thallium (ion or complex); I = excited state of thallium.

that Seitz's energy level scheme cannot explain the visible luminescence of the phosphors. Bose and Sharma have also discussed this point. Any energy level scheme which explains the visible part of luminescence must take into consideration the transfer of energy from thallium levels to the valence levels of the ions building up the lattice.

Such a scheme has been presented in Fig. 4. The ionic exciton levels L_1, L_2, .., lie between the valence and the conduction bands, and are responsible for lattice emission. The impurity levels are so situated in a perturbed crystal that a transition from one of them directly to its ground state gives rise to the characteristic emission of thallium, and to the ionic states go to enhance the lattice emission bands, *e.g.*, in case of KCl-Tl. Except in case of NaBr-Tl, the impurity levels do not lie at the same height as those of lattice levels, hence the characteristic emission is on the shorter wavelength side, while in case of NaBr-Tl, they distinctly overlap. The transfer transitions from thallium exciton (?) levels (be it due to complex formation, or to substitution at vacant anion sites) are distinctly responsible for exhibiting very wide, extended, and unresolved emission regions in case of NaBr-Tl and KBr-Tl.

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Khaira Laboratory of Physics,
Calcutta University.

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